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PROCEEDINGS
OF THE
NATIONAL ACADEMY OF SCIENCES
Volume 5 AUGUST 15, 1919 Number 8

SOME APPLICATIONS OF THE VARIATION OF HYDROGEN OVERVOLTAGE WITH THE PRESSURE

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Communicated by A. A. Noyes, June 2, 1919

In a previous communication[1] it was shown that the hydrogen overvoltage at a given electrode can be expressed, at low current densities, with a considerable degree of approximation, by the equation:

$$2\,F\,E = \frac{3RT}{pr}\,\gamma$$

in which E, r, p, and γ are, respectively, the overvoltage, the radius of the hydrogen bubbles, the pressure, and the surface tension. The value of r was found experimentally to be independent of the pressure, and a plot of the variation of the overvoltage with the pressure was found to follow, very nearly at least, the hyperbola required by the above expression.

It next became interesting to investigate some chemical processes in which hydrogen overvoltage is intimately involved in order to see whether changes in these processes, produced by variations in the external pressure, are also in the direction predicted by the theory. Three such processes are: (1) the corrosion of metals in acid solutions, (2) reduction in acid solutions by metals, and (3) the electrodeposition of metals.

1. Metal Corrosion.—When a metal above hydrogen in the electromotive series is placed in a solution of an electrolyte there is a tendency for the metal to ionize; i.e., to split into ions and electrons; for instance, with iron, the following reaction tends to take place

$$\mathrm{Fe} = \mathrm{Fe}^{++} + 2e, \qquad (1)$$

(e = electron). However, no chemical action will ensue unless another reaction, involving the absorption of the electrons liberated in Reaction 1, can also occur. In the absence of oxidizing agents the only possible reaction is

$$2H^+ + 2e = H_2 \tag{2}$$

Any factor which tends to decrease the velocity of Reaction 2, i.e., which increases the overvoltage, will decrease the corrosion represented by Reaction 1. Watts and Whipple[2] have found that, contrary to statements in the chemical literature, a decrease of the external pressure will produce a decrease of corrosion of metals in acids. These workers, however, attribute the decreased corrosion to the absence of air in the solutions which were under reduced pressure. As it seemed probable to us that the effect is, largely at least, due to an increase in the overvoltage with decreased pressure, we repeated their experiments, taking care to exclude oxygen from the acid. Table 1, which contains typical results for Zn, Fe, and Cd, shows that the effect of decreased pressure on the corrosion of the first two of these metals is in the direction predicted. No bubbles of hydrogen were observed to leave the surface of the cadmium, so no change of overvoltage, and therefore no change of the corrosion, with the pressure is to be expected.

TABLE 1

METAL	LOSS IN WEIGHT	
	At 1 atmospheric pressure	At $\frac{1}{10}$ atmospheric pressure
	gram	*gram*
Zn	0.0927	0.0594
Fe	0.0797	0.0469
Cd	0.0018	0.0018

2. *Reduction, in Acid Solutions, by Metals.*—On placing a strip of iron into a slightly acidified solution of $FeCl_3$ the metal enters solution according to Reaction 1. The two ionic reactions that compete, so to speak, for the liberated electrons are

$$Fe^{+++} + e = Fe^{+++} \tag{3}$$

and Reaction 2. Here we can predict that a decrease of pressure will, by increasing the overvoltage, reduce the velocity of Reaction 2, with the result that Reaction 3 will be favored. The experimental results of a series of measurements are plotted in figure 1, in which abscissas represent pressures and ordinates reduction in a given time. Due to irregularities in the surface of the iron the points are scattered, but the trend is clearly the same as that of the overvoltage-pressure curves given in the previous paper. This appears to be a promising method of increasing the speed and efficiency of a large class of reductions.

3. The Electrodeposition of Metals.—If hydrogen were evolved at a cathode at its reversible potential under all conditions no metal higher in the electromotive series than hydrogen could be deposited electrolytically from an aqueous solution. Due to hydrogen overvoltage, however, it is possible to obtain deposits of these metals as high in the series as zinc. The current efficiency of such a deposition depends, mainly, upon the relative magnitudes of the potential between the solution and the metal, and the hydrogen overvoltage of the metal; the efficiency increasing, of course, with an increase of the overvoltage. The figures in table 2 indicate that the increase of hydrogen overvoltage produced by a decrease of pressure is accompanied, in the case of the deposition of zinc, by an increase in the efficiency of the deposition. These depositions were all made from the same solution, and at the same current density and temperature.

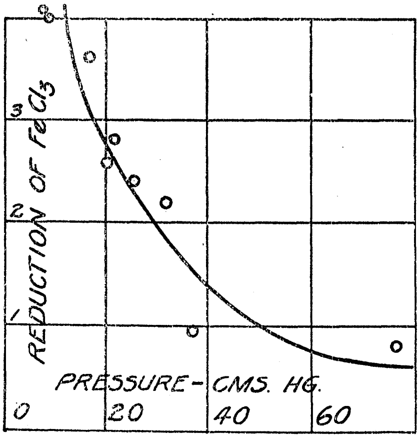

FIG. 1

TABLE 2

Pressure, *cms. Hg*	76	13	12	6
Efficiency, *per cent*	75	81	92	97.5

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[1] These Proceedings, May, 1919, also *J. Amer. Chem. Soc.*, 41, 1919, (194).

[2] *Trans. Amer. Electrochem. Soc.*, 32, 1917, (257).